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EFFECT OF ADSORBED WATER FILMS ON THE VAN DER WAALS
FORCE BETWEEN QUARTZ GLASS SURFACES

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1. Introduction

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In a previous work [1] we were able to make an accurate calculation of the Van der Waals force using the absorption spectrum of quartz, which had been measured across a wide wave-length range shortly before [2]. In particular, it was shown that the infrared spectrum of quartz glass is essentially affected only by the Van der Waals constant B, and hardly at all by the Van der Waals constant A. At the time, we were able to report briefly on the first measurements, which confirmed the theory. In the following we report further results which were obtained with the method described in [1]. In particular, we intended to study the effect of adsorbed water films on the Van der Waals interaction.

2. Performance of the Experiments

2.1 Measuring methods

Aside from attempts to determine adhesion, two methods have previously been developed to measure the Van der Waals force at short distances (d <' 1,000 Å). Baily [3] split a thin platelet of mica and then held the two parts separated at one end by a ball after recombining them. The Van der Waals force was determined

[*] Numbers in the margin indicate pagination in the original foreign text.

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Front side

Back side

Calibration mark ──── Zero line

Aluminum reflecting coating
Quartz platelet
Aluminum bar
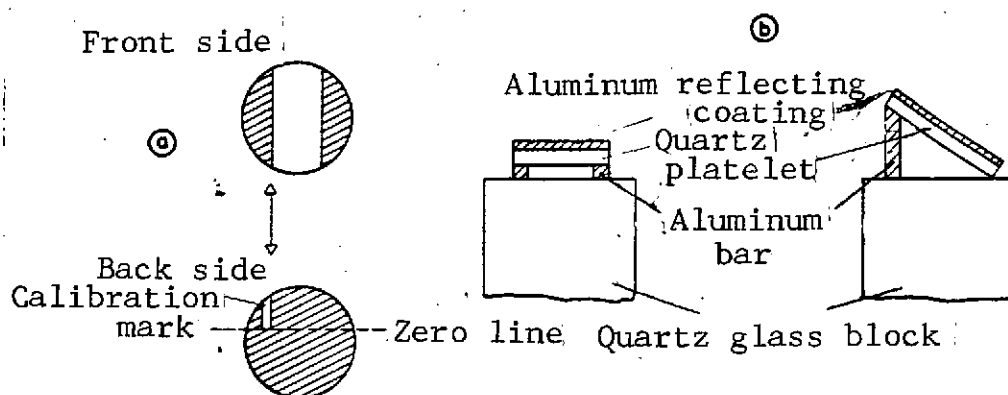Quartz glass block

Figure 1. (a)   Geometric arrangement of the vapor-deposited surfaces
                (shown cross-hatched) on the quartz glass platelets
                used. One or two crossbars, as chosen, are vapor-
                deposited on the front. A calibration mark is placed
                on the back for performing the null measurement
                reproducibly, and for the following determination
                of the deflection.
        (b)   Schematic representation of the two different methods
                for measuring the deflection of a thin platelet.
                The platelet has two vapor-deposited cross-bars at
                the left, and one at the right.

from the resulting deformation, or curvature, of the platelets.
Tabor and Winterton [4] developed another method in which the test
bodies, facing each other in the form of crossed semicylinders,
spring into contact at a certain distance. This occurs when the
attractive force between the bodies becomes greater than the
restraining force of the elastic spring on which one of the two
test bodies hangs. Sparnaay and Jochems previously reported a
similar technique [5].

The method which we have developed is relatively simple in
principle, and has been described extensively already [6]. A thin
quartz platelet, polished on both sides, is laid on a quartz block
having a radius of curvature, $r > 10^5$ cm. One side of the platelet

is made reflective with vapor-deposited aluminum. One or two cross-bars of aluminum, as selected, are deposited on the other side (see Figure 1). The Van der Waals force to be studied causes the platelet to bend, and the bending can be measured with an interference microscope.

2.2 Preparation of the Platelets

After careful cleaning the platelets, which are about 40 µm thick, are vapor-coated with aluminum over all of one side (reverse side), except for a reference area, as shown in Figure 1. Then a null measurement is made. The quartz platelet is placed with its yet untreated side (front side) on the quartz glass block. Then a zero line is measured interferometrically, perpendicular to the long edge of the calibration mark. That is, <u>/ 506</u> one determines the slope K of the reflecting surface with respect to a reference plane of the interference microscope. At the same time, this zero line is also perpendicular to the bars which are vapor-deposited at the next step. If the platelet is now laid on the glass block again, there is a deflection because of the forces acting between the two solid bodies. The interferogram at the calibration line is measured again. From the change in separation of the interference bands, one obtains the change in the slope of the line of deflection.

The solid line in Figure 2a corresponds to the zero line. It gives a statement about the change in thickness of the plate-let, about its roughness, and about deviation from planarity. As a rule, the platelets were slightly wedge-shaped. Also, one can compensate for a slight bending due to the weight of the platelet itself by a measurement at large distances. The dashed line shows the change in the slope after vapor-depositing the cross-bars.
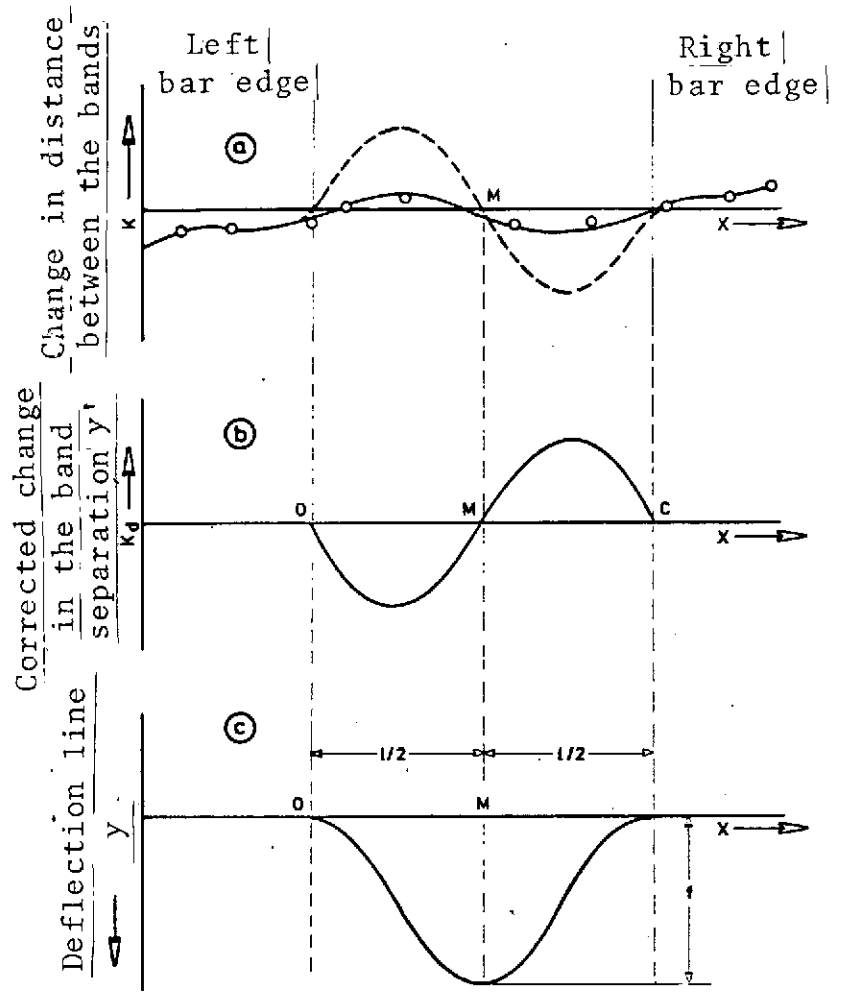
Figure 2 (a) Schematic representation of the change in the band
separation of the interference lines as a function of
the position coordinate x.   The result of the null
measurement is plotted with a solid line.   The
change produced by the deflection of the platelet is
shown as a dashed line.

(b) The change in the band separation, y', corrected by
using the zero measurement, as a function of the
position coordinate.

(c) The bending line y determined from the change of
the band pattern.

The differentiated deformation line (Figure 2b) represents the difference between the two curves. For reasons of symmetry, it is necessary that

$$\left| \int_0^{M} g(x)\,dx \right| = \left| \int_M^{C} g(x)\,dx \right|, \qquad (1)$$

where $K_d = y' = g(x)$.

Figure 2c, finally, shows the bending y of the platelet. In order to determine the force, q, per unit of length from that, we must solve the general differential equation

$$q = EI\,\frac{d^4 y}{dx^4} \qquad (2)$$

In Equation (2), E is the modulus of elasticity for the material used; I is the polar moment of inertia with respect to the neutral axis; y is the deflection; and x is a position coordinate (extent of the sample perpendicular to the vapor-deposited bars). A computer program was used to solve this equation with the experimental values. By means of a Fit Program, a polynomial of the M-th degree was fitted to a given series of measurements by the method of least squares:

$$y = P(1) + P(2)\,x + P(3)\,x^2 + \cdots + P(M)\,x^{M-1}. \qquad (3)$$

2.3 Control of the sample objects

In order to obtain definite and reproducible results in the measurement of the Van der Waals force, it is extremely important to keep the measured object as clean as possible. A cleaning method was selected which has already proved itself in the fields of surface and semiconductor physics, and which is also described in a similar form in the literature [7]. In order to test the
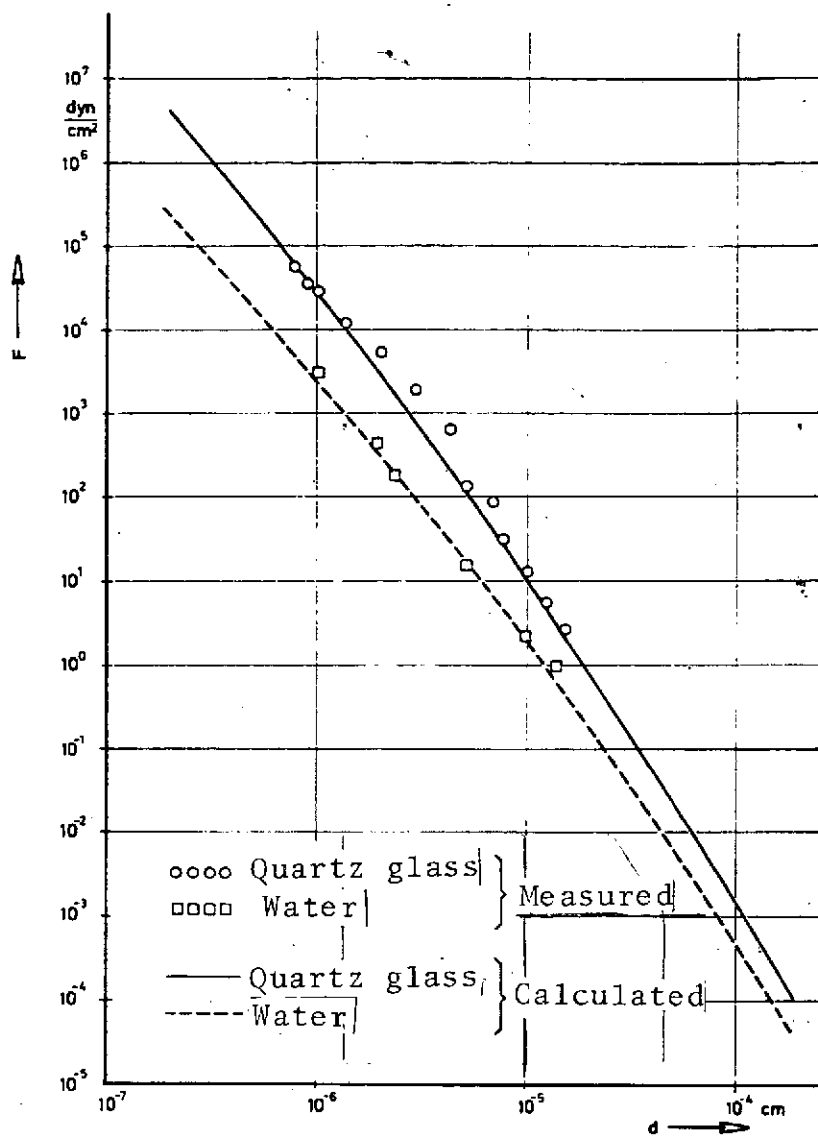
Figure 3. Calculated and measured Van der Waals force acting per
unit of surface area, as a function of the separation.
The results of the measurement at 95% relative
humidity are compared with the values calculated for
water.

cleanliness of the surfaces, the water break test [8] and an electronic component test [9] were performed.

2.4 Discussion of the methods of measurement

Along with the force, the separation d of the bodies in particular enters into the determination of the Van der Waals constants. In our method, a certain distance range is firmly prescribed. The distance can be determined with sufficient accuracy using modern measuring instruments ($\Delta d < 50 \text{Å}^1$). The error, then, is primarily in the determination of the force. The measurement limit is reached here in one case if the weight of the quartz platelet itself causes deformation of the same order of magnitude as does the Van der Waals force. The measurement error also becomes very large if the change of slope of the sample in the stressed state becomes so small that the resolving limit of the interference microscope is reached. With the two experimental arrangements used, the measurement error can amount to as much as 100% at distances below 1,000 Å and platelets with bars at two sides.

With platelets having two bars, we get a particularly accurate statement of the quality of the measurements, because the following points can easily be tested: the deflection curve must be a parabola, to a good approximation, with the branches leaving the center of the sample symmetrically; furthermore, the inflection points of the deflection curves must be symmetrical to the endpoints. From this test, we can determine whether disturbances are present due to impurities or inadequate sample surface. One gets more information about the dependence of the Van der Waals force on the distance of the interacting surfaces in one measurement from plates with one bar; but the just-mentioned possibilities for testing the result are lacking. The quality of this series of measurements is determined from their reproducibility, on one hand, and on the other hand from the agreement in individual

regions of measurement with the results obtained with quartz platelets having two vapor-deposited bars. An extensive estimation of errors can be found in reference [5].

3. Results

3.1 Force as a function of the distance

The results of determination of force per unit area as a function of the distance between the solid bodies are plotted in Figure 3. At a relative humidity of about 1% for the ambient air, the force is inversely proportional to the fourth power of the distance at a distance of more than 1,000 Å, and inversely proportional to the third power of the distance at distances less than 150 Å. In between there is a transition region, in which the force must be expressed by the following expression [1]:

$$F(d) = \frac{\hbar}{2\pi^2 c^3} \int\limits_0^\infty d\omega \int\limits_0^\infty dp\, p^2\omega^3 \left[\varepsilon_3\,(i\omega)\right]^{\frac{3}{2}}$$

$$\times \left[\frac{(s_1 + p)(s_2 + p)}{(s_1 - p)(s_2 - p)}\exp\left(\frac{2p\omega d\left[\varepsilon_3\,(i\omega)\right]^{\frac{1}{2}}}{c}\right) - 1\right]^{-1}$$

$$+ \left[\frac{\left[s_1 + p\varepsilon_1\,(i\omega)/\varepsilon_3\,(i\omega)\right]\left[s_2 + p\varepsilon_2\,(i\omega)/\varepsilon_3\,(i\omega)\right]}{\left[s_1 - p\varepsilon_1\,(i\omega)/\varepsilon_3\,(i\omega)\right]\left[s_2 - p\varepsilon_2\,(i\omega)/\varepsilon_3\,(i\omega)\right]}\right.$$

$$\left.\times \exp\left(\frac{2p\omega d\left[\varepsilon_3\,(i\omega)\right]^{\frac{1}{2}}}{c}\right) = 1\right\}^{-1}\right\}. \tag{4}$$

This result agrees with the theoretical estimates which have been made by various authors [1, 11, 12]. A similar curve shape also appeared with measurements done on mica [4, 13]. If we change the water vapor pressure around the sample, and thus change the amount of adsorbed water, the Van der Waals force decreases. At the same time the range in which the force curve can be approximated by functions proportional to $1/d^3$ and $1/d^4$ also changes. If we consider

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the point of intersection of the lines which appear in a log-log presentation of the two increases just mentioned, we see that this intersection point shifts to larger distances between the solid bodies with increasing relative humidity. The curve for the force as a function of distance can be estimated only by considering the five-body system quartz glass - water - water vapor - water - quartz glass. A computation for this system would be necessary for quantitative interpretation of the measurements. For this, of course, it would be necessary to consider the change of the dielectric constant of water in a surface liquid film. The calculated curve for the Van der Waals force per unit surface as a function of the distance which is obtained if we base the evaluation only on the absorption spectrum of water, according to reference [14] is also plotted in Figure 3. For purposes of comparison, the experimental results obtained at a relative humidity of about 95% are plotted in Figure 3. At this humidity we can proceed on the basis that a layer having an average thickness of about three to four molecular layers is adsorbed on the quartz surface [15]. In spite of these very simplified assumptions, we obtain a surprising agreement between theory and experiment. Careful theoretical study of this complex system is still lacking.

3.2 Determination of the Van der Waals constants A and B

From the theory, it is to be expected that the attractive force F decreases as a function of the distance d as $F = B/d^4$ at very large distances between two solids, and as $F = A/d^3$ for very small distances.

In the corresponding regions, the experimental values can can be matched approximately by the representation with line segments selected in Figure 3. From this we can determine the constants A and B without difficulty.
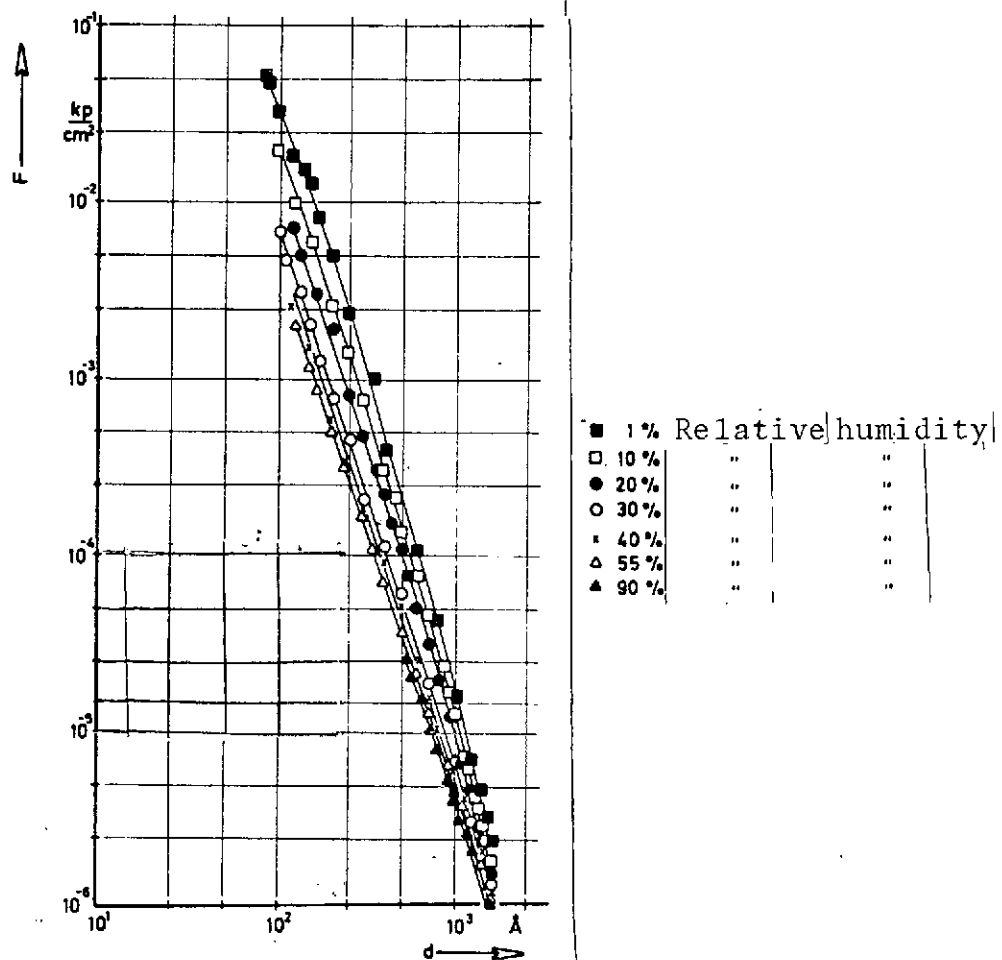
Figure 4. The attractive force per unit area between two solid surfaces as a function of the distance. The relative water vapor pressure at which the corresponding experiment was done is plotted as a parameter.
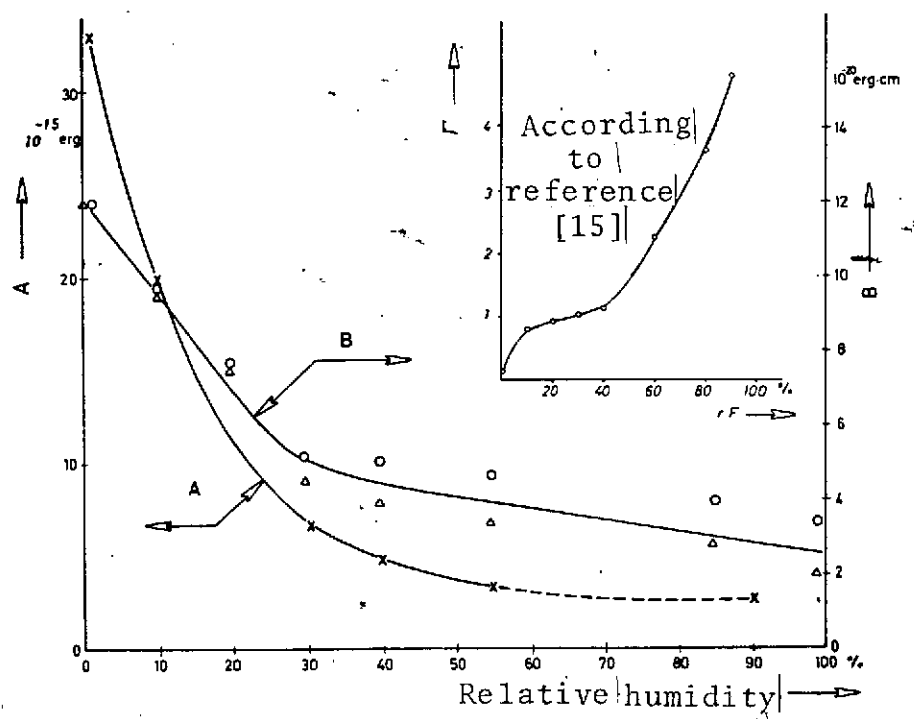
Figure 5. The Van der Waals constants A and B of quartz glass as a function of the relative humidity of the environment in which the experiment was performed. The results from two series of measurements were plotted to determine B. In the upper right corner, the thickness of the adsorbed layer, according to Reference [15], is plotted versus the relative humidity.

The following values were found for quartz in a dry environment (about 1% relative humidity and 20°C) and with adsorbed water (about 35% relative humitidy):

	A (erg)	B (erg cm)
Quartz	33×10^{-15}	12×10^{-20}
Water	3.3×10^{-15}	2×10^{-20}

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As already appears from Figure 4, the attractive force decreases as the relative humidity of the environment increases. That is, the attractive force decreases rapidly with increasing thickness of the adsorbed water layer. The constants A and B are plotted as functions of the relative humidity of the air in Figure 5. (The water vapor sorption isotherm of quartz glass, according to reference [15], is also shown in the upper right corner of Figure 5). According to this, less than a monolayer of water is already enough to make the value of B to fall to half its initial value. It can be seen that this drop is closely related to the change of surface energy as a result of adsorption. This dependence should be taken into consideration in comparing different measurements.

4. Relation Between Van der Waals Force and Surface Energy

The surface energy of a material can be defined in such a way that one can understand it to be half the work that must be done   /513 to split it; that is, to overcome the intermolecular forces by making new surfaces. Proceeding from this, Krupp has shown with elementary means that, to a good approximation, the Van der Waals force is directly proportional to the surface energy for molecular crystals [14]. Bangham [16] has described an expression which describes the change of the surface energy as a function of the thickness of a sorbate layer:

$$\Delta F = \sigma_0 - \sigma = - RT \int_0^P \Gamma \, d(\ln[p]). \qquad (5)$$

Here σ_0 is the surface energy of a material in vacuum, and σ is the surface energy of the same material if the sorbate layer thickness is Γ at a vapor pressure p. In another work, Setzer [17] has determined the change of the surface energy of a solid material, calcium silicate hydrate, from the sorption isotherms. The change of the surface energy determined by Setzer [17] is
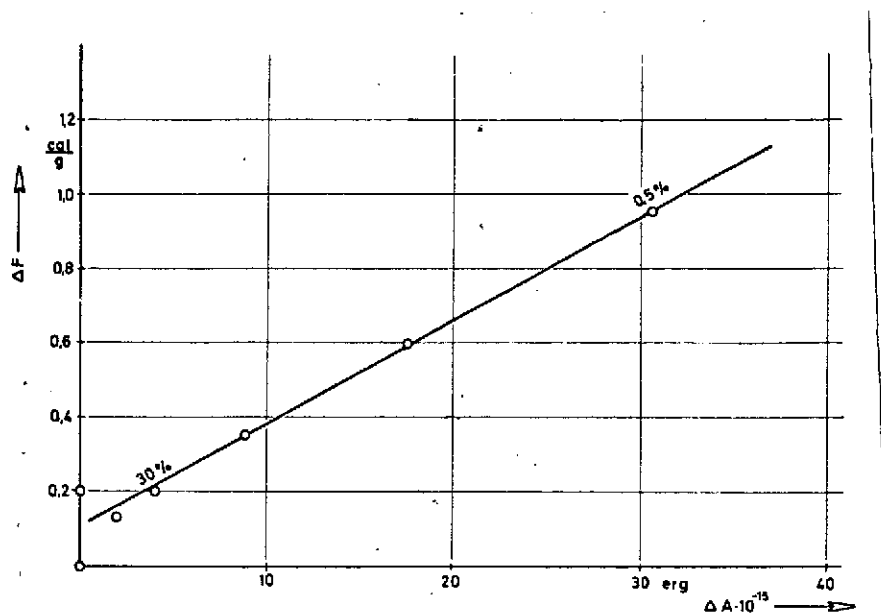
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Figure 6. Change in the surface energy, calculated from the sorption isotherm, plotted versus the change in the Van der Waals constant A. The corresponding relative humidity is indicated in percent.

plotted versus the change of the Van der Waals constant A, determined at the same relative humidity, in Figure 6. The relative humidity of the air is indicated in percent in Figure 6. We see from this that there is actually a linear relation over a wide range, within the limits of measurement accuracy.

If we consider the change of the surface energy as a function /514 of the layer thickness r, it is striking that we can note a steep drop up to a bimolecular coating, while the amount of water adsorbed beyond that has comparatively little effect. In the future we shall be concerned with the quantitative description of these relations.

REFERENCES

1. Wittmann, F., H. Splittgerber and K. Ebert. Z. Physik, Vol. 245, 1971, p. 354.

2. Platzöder, K. Dissertation. Universität München 1969.

3. Bailey, A. Dechema Monograph. Vol. 51, 1964, p. 21.

4. Tabor, D. and R.S.H. Winterton. Nature, Vol. 219, 1968, p. 1220.

5. Sparnaay, M.J. and P.W.J. Jochems. In: Proc. Third Intern. Congr. on Surface Acitivity. Köln, Vol. II, Section B, 1960, p. 375.

6. Splittgerber, H. Dissertation, Techn. Universität Munchen, 1971.

7. Haereus, Fa. Mitteilung Q-A 3/131.

8. Farnsworth, H.E. Clean Surfaces. Wiley, New York, 1960, pp. 107 - 135.

9. Zerbst, M. and H.E. Longo. Z. Angew. Physik, Vol. 19, 1965, p. 85.

10. Dzyaloshinskii, J.E., L.P. Lifshitz and L.P. Ptaevskii. Advan. Phys., Vol. 10, 1961, p. 165.

11. Hunklinger, S. Dissertation. Techn. Universität München, 1969.

12. Ebert, K. and F. Wittmann. Phys. Letters 32A, 1970, p. 289.

13. Tabor, D. and R.S.H. Winterton. Proc. Roy. Soc. (London) Vol. 312, Series A, 1969, p. 455.

14. Krupp, H. Advan. Colloid Interface Sci. Vol. 1, 1967, p. 2.

15. Hackermann, N. and A.C. Hall. J. Chem. Phys. Vol. 62, 1958, p. 1212; Shdanow, S.P. Ber. Akad. Wiss. UdSSR, Vol. 120, 1958, p. 103.

16. Bangham, D.H. Trans. Faraday Soc. Vol. 33, 1937, p. 805.

17. Setzer, M. Dissertation, Techn. Universität München, 1972.

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16. Abstract

A method to determine Van der Waals forces at low distances is described. Results of experiments carried out with adsorbed water films are in excellent agreement with the theory of Dzyaloshinski. The thickness of adsorbed water films has been varied by changing the vapor pressure of the surrounding atmosphere. The influence of thickness of adsorbed water films has been studied. At high relative humidities the attractive force can be calculated with the help of Dzyaloshinski's theory by using the dielectric properties of water. The experimentally determined Van der Waals force is discussed in relation to the surface energy of the interface.

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